

Fluorescence Spectra of Anthracene Dissolved in Vinylic and Olefinic Polymers

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Neste trabalho se apresenta uma revisão sobre as aplicações do antraceno como sonda molecular para acompanhar processos e determinar temperaturas de relaxações em polímeros. Descrevem-se também algumas propriedades fotofísicas do antraceno que são importantes para determinar o tamanho e caracterizar o tipo de domínios no polímero sólido onde a sonda molecular está localizada. Tem-se demonstrado que o antraceno dissolvido em polietileno de baixa densidade apresenta um espectro de fluorescência com uma estrutura vibrônica bem resolvida, em temperaturas baixas. Nos casos do antraceno dissolvido em poli(acetato de vinila), poli(cloreto de vinila) e poliestireno, observou-se uma resolução vibracional menor devido ao acoplamento dos modos vibracionais fora do plano da sonda com matrizes poliméricas. Essas características espectrais relacionadas com a estrutura vibrônica da fluorescência do antraceno são dependentes tanto da rigidez quanto das dimensões dos volumes livres das matrizes.

In this work we present a review of the applications of anthracene as a fluorescent probe to follow relaxation processes and to determine the temperature of relaxation processes in different polymers. We also describe some photophysical properties of anthracene that are important to determine the size and to characterize the type of domains in the solid polymer where the molecular probes are localized. We have demonstrate that anthracene dissolved in low density polyethylene exhibits a well-resolved vibronic fluorescence spectrum at low temperatures. In the case of anthracene dissolved in poly(vinyl acetate), poly(vinyl chloride) and polystyrene we observed low vibronic resolution due to the coupling of out-of-plane vibrational modes of the probe with polymer matrices. These spectral characteristics are related to the vibronic structure of the anthracene fluorescence, which is also dependent on both the rigidity and dimensions of the free volumes of the matrices.

Keywords: anthracene, fluorescence spectra, vibrational resolution, polymers

Introduction

Applications of luminescence spectroscopies as tools to study synthetic polymers and polymer blends are useful to understand different properties of both the bulk and the surface of the samples. The merit of the luminescence probes in these studies can be summarized: high sensitivity, nondestructiveness, possibility of several different types of measurements with only one dye, information on the interactions over a wide range of radii and time, etc.¹⁻⁴

The applications of luminescent molecules to study secondary relaxations of polymers and polymer blends are possible by the high sensitivity of the luminescent mole-

cules to the microenvironment of the polymer matrix. In this case the intensity of the emission (in a photostationary experiment), the emission decay profile (in a time-resolved experiment), or a time depolarization function of the molecular luminescent probes or labels depend on their intrinsic photophysical properties and their interactions with the polymer matrices¹⁻⁹.

In order to support the studies of secondary relaxations of polymer and polymer blends using luminescence spectroscopies, it is important to establish the spectral characteristics of the luminescence of molecular probes or labels and their dependence on the microdomains of the matrices. In this work, we present a review of the fluorescence

spectra of anthracene dissolved in different polymers in order to make correlations between the vibronic structure of the emission bands and the types of the domains and how polymer relaxation processes may be followed by changes in the intensity of the fluorescence signal.

Experimental Details

Anthracene (AN, Carlo Erba) was used as received. Commercial poly(vinyl chloride) (PVC) was from Fluka, with molecular weight $M_w = 68,000$ g/mol and polydispersity 1.1^{9,10}. High molecular weight poly(vinyl acetate) (PVAc), $M_w = 237,000$ g/mol, polydispersity 1.1 was from Aldrich Chemical Co.¹¹ Polystyrene (PS) was from EDN - Poliestireno do Norte Ltda., with molecular weight $M_w = 230,00$ g/mol. Their molecular weights and polydispersities were determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as a solvent and polystyrene standards. Low density polyethylene (LDPE) blown film, 38 μm thick, was from Poliolefinas, without additives, and was washed with methanol before using.

Films of PVC, PVAc and PS containing AN were prepared by casting a solution in dichloroethane on a glass plate. The solvent was evaporated at room temperature and the samples were stored under vacuum. The amount of polymers dissolved was established in order to obtain fluorescence spectra in the film equivalent to 10^{-5} M of AN and dissolved in a non-viscous solvent to prevent aggregation of the probe in the matrices. AN was incorporated in LDPE matrix by swelling the film in a solution 10^{-3} M in *n*-hexane.

Luminescence measurements at various temperatures were recorded using the equipment described earlier¹¹⁻¹³. Thermograms and X-ray diffraction patterns were obtained as described earlier⁷⁻⁹.

Results

Electronic spectra of anthracene in LDPE

The electronic absorption spectrum of AN (D_{2h}) is composed of two electronic transitions in the 25,000-40,000 cm^{-1} range (400-200 nm). The lower energy transition has been observed at $\sim 25,000$ cm^{-1} and is assigned to the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ (β -band) with the transition moment polarized along the short molecular in-plane axis. This transition contains a well-resolved vibrational structure involving totally symmetric vibrational modes of 390 cm^{-1} and 1401 cm^{-1} . The second electronic absorption band ($\sim 40,000$ cm^{-1}) is assigned to the ${}^1B_{3u} \leftarrow {}^1A_{1g}$ (α -band) transition, and is polarized along the long molecular axis. In general, this transition is not observed in the electronic absorption spectra since it overlaps with the β -band^{14,15}.

The fluorescence spectrum of AN is assigned to the transition ${}^1A_{1g} \leftarrow {}^1B_{2u}$, and presents a well-resolved vibrational structure involving totally symmetric modes of 403

cm^{-1} and 1416 cm^{-1} . The position of the purely electronic 0,0 transition and the vibronic resolution of the fluorescence spectrum are strongly dependent on the medium, on the temperature^{16,17} and on the concentration¹⁸. If the solvent is appropriate, the fluorescence spectra of AN at low temperatures, will be composed of a vibronic progression of narrow bands, often called "quasi-line", and diffuse bands, repeating the general energy distribution in the spectrum and superposed on the "quasi-line" one¹⁹. Quasi-line fluorescence spectra of AN may be obtained in solid *n*-heptane solutions, at low temperatures and low concentrations²⁰. As pointed out by Shpol'skii the quasi-line spectrum should be obtained if the dimension of the longest axis of the guest molecule is similar to the length of the host molecules. Some quasi-line spectra exhibit a multiplet structure as a result of different positions of the guest molecule in the host crystal structure^{17,19}.

In Fig. 1. are shown absorption (at room temperature) and fluorescence (at 15 K) spectra of AN dissolved in LDPE. We observe in these spectra that:

- i) the fluorescence spectrum is a specular image of the absorption band;
- ii) there is a strong overlap between the absorption and emission bands;
- iii) the fluorescence spectrum is composed of a vibronic progression, which can be described by a series of bands polarized along the short axis:

$$\nu_M = \nu_{0,0} - n_1\nu_1 - n_2\nu_2 \quad (\text{cm}^{-1}) \quad (1)$$

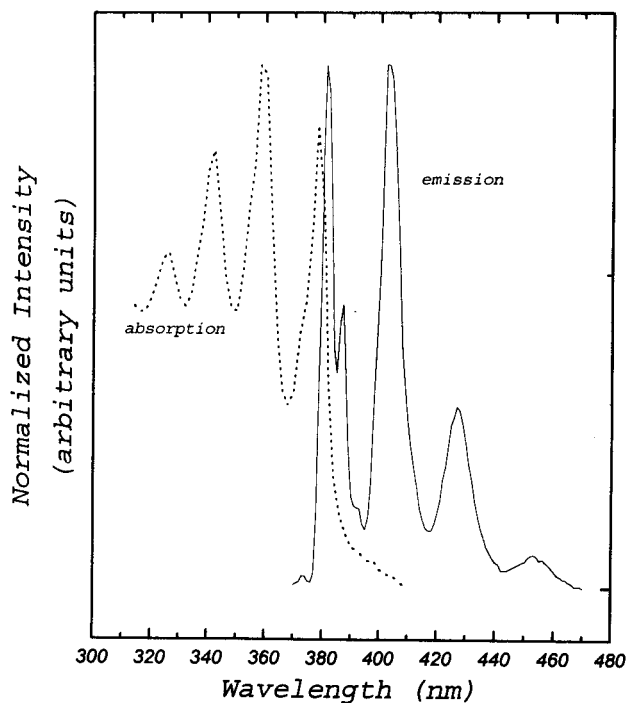


Figure 1. Absorption (room temperature) and fluorescence (15 K) spectra of AN dissolved in LDPE. ($\lambda_{\text{exc}} = 340$ nm).

where: $\nu_{0,0}$ is the purely electronic 0,0 transition; $\nu_1 \cong 1400 \text{ cm}^{-1}$ and corresponds to the totally symmetric C-C stretching vibration with $n_1 = 0, 1, 2, 3$ and 4; $\nu_2 \cong 396 \text{ cm}^{-1}$ and corresponds to the skeletal distortion of symmetric a_{1g} mode with $n_2 = 1, 2$; and a series of bands polarized along the long axis, with very low intensity²¹;

iv) the band at $\sim 381 \text{ nm}$ of AN in LDPE corresponds to the purely electronic 0,0 transition and that at $\sim 387 \text{ nm}$, which is well-resolved in this case, may be assigned to $\nu_M = \nu_{0,0} - 400 \text{ (cm}^{-1}\text{)}$. We also observed the vibrational progression corresponding to $\nu_M = \nu_{0,0} - n_2 1400 \text{ (cm}^{-1}\text{)}$. This resolution is only observed if the AN molecules are incorporated in a rigid phase of the matrix in such a way that the non-radiative deactivation processes involving out-of-plane vibrational modes and intermolecular interactions are inhibited.

These results indicate that LDPE in the solid state at 15 K should contain rigid cages of the same dimension as the AN molecules¹⁶. The dependence of the relative intensity of the band at $\sim 387 \text{ nm}$ and that of the pure electronic 0,0 transition in different media or temperatures allows us to establish some energy transport mechanisms of AN in the electronically excited singlet state.

Fluorescence spectra of AN in PS, PVAc and PVC

The fluorescence spectrum of AN dissolved in PVAc is shown in Fig. 2. It is also composed of a vibronic progres-

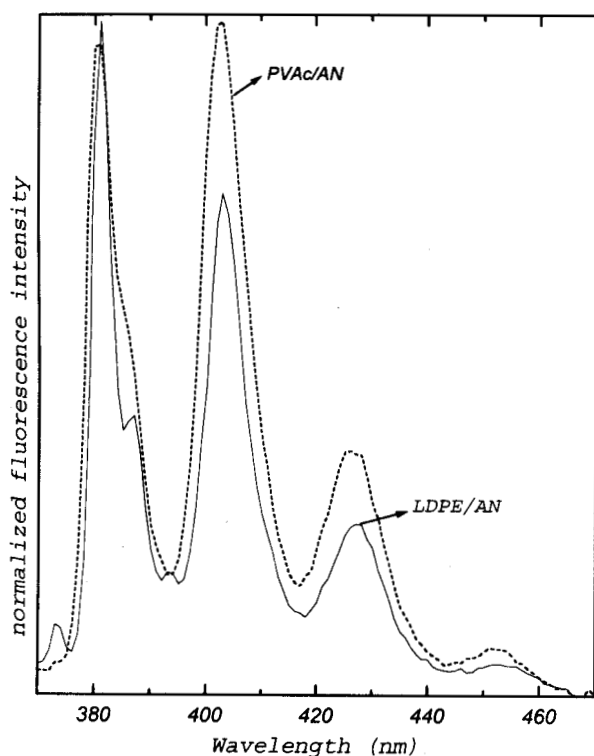


Figure 2. Fluorescence spectra at 15 K of AN dissolved in PVAc (----) and LDPE (—) ($\lambda_{exc} = 340 \text{ nm}$).

sion and may be assigned to isolated molecules, as indicated by the relative intensities of the bands centered at $\sim 380 \text{ nm}$ and $\sim 402 \text{ nm}$. Moreover, this spectrum can also be described by a progression like that defined in Eq. 1, although it is not possible to resolve the band at $\nu_M = \nu_{0,0} - 400 \text{ (cm}^{-1}\text{)}$, as in the case of AN dissolved in LDPE at the same temperature $T = 15 \text{ K}$. As pointed out earlier, this vibrational band is only present if the molecule is incorporated in a rigid phase of the matrix in such a way that the non-radiative deactivation processes involving out-of-plane vibrational modes and intermolecular interactions are inhibited. Although PVAc at 15 K forms a rigid matrix, the presence of a large lateral group (acetate COOCH_3) in the polymer chain leads to free-volumes being available to AN guest molecules, which are not similar to that in a Shpol'skii solvent or polymer matrix like LDPE. Therefore, some non-radiative pathway related to the out-of-plane vibrational modes of low frequencies should be activated. Similar results have been obtained for AN dissolved in poly(vinyl chloride) ($-\text{CH}_2 \text{CHCl}-$)_n and polystyrene ($-\text{CH}_2-\text{CH}\phi-$)_n ($\phi = \text{phenyl group}$).

Microdomains in polymers

The X-ray scattering patterns of LDPE samples are composed of two crystalline peaks assigned to the reflections of indexes (110) and (200) and one wide scattering band at $2\theta = 20.5^\circ$ assigned to the amorphous phase. These diffractograms show that the structure of the crystalline phase of PE is orthorhombic. The crystallinity degree can be calculated either by DSC or by the relationship between the amorphous and crystalline X-ray diffraction patterns. We observe no distortion of the crystalline structure of PE samples containing AN, indicating that this probe was not located within the crystalline phase of the polymer. Therefore, the studies of relaxation processes of polymers and polymer blends using photoluminescence methods must consider the place where the probes or labels are localized.

Aromatic condensed hydrocarbon molecules (like AN) dissolved in semicrystalline polymers (like LDPE) may be preferentially located in two different sites: in the amorphous phase and on the surfaces of the crystallites^{22,23}. The proportions of each are based on the Peterlin general model for the morphology of PE²⁴. Phillips et al. reported dielectric relaxation studies of aromatic molecules in different types of PE and concluded that a) the β and γ relaxation processes are clearly associated with an amorphous phase that is oriented by stretching the matrix; b) they are most likely in the interfibrillar amorphous material; c) the γ process involves short-range motions of the chains and takes place over a distance between 2.5 \AA and 4.3 \AA ; and d) the β process permits a significant component of spinning about the longest axis of the aromatic molecules²³.

Similar results were obtained for the deactivation processes using luminescent probes, suggesting that γ -relaxation of LDPE involves motions of short segments of polymer chains, while the β process involves motions of longer segments of the chains. The latter should be at least as long as the longest axis of the molecular probes (at least seven methylene units in the case of anthracene)⁷⁻¹⁰.

Other experiments using different approaches (chemical and photochemical reactions of guest molecules in polymers and diffusion of solute molecules in LDPE films) have made important contributions to establish changes that occur to the size, shape and distribution of dopant sites in stretched and unstretched LDPE films^{2,25-27}. These studies indicate that:

- i) different site types may exist in LDPE;
- ii) the sites provided to dopant molecules are reduced in volume and the guests may change their localization during film stretching;
- iii) the distribution of free volumes for sites in stretched films is much narrower than in unstretched ones.

From these results we could consider that a LDPE matrix, a semicrystalline polymer, is composed of at least two domains where AN molecules may be localized: the amorphous domains and the surfaces of the crystallites.

On the other hand, the samples of PS, PVAc and PVC used in this work are completely amorphous, as determined by DSC and X-ray diffraction. However, amorphous domains of a polymer are not homogeneous. There are many spectroscopic data showing that amorphous domains of polymers present a free-volume distribution^{2,4,28}. One example of these results was obtained by the determination of the temperature dependence of photo- and thermal E-Z isomerization of the photochromic *p*-dimethylaminoazobenzene (DAB) dissolved in poly(vinyl acetate). The kinetics of the photo- and thermal reactions were investigated in a temperature range from below 18 °C to above 40 °C, passing through the glass transition temperature of this polymer (28 °C). The activation energies in the two temperature regimes could be calculated from the first-order rate constants. The thermal reactions of DAB in PVAc films were found to decay with a single exponential function at $T > T_g$. However, at $T < T_g$, at least two exponential terms were required to analyse the reaction kinetics. These results were explained by considering that below T_g , the thermal reaction is cooperative with the generation of free-volumes²⁹. Our results are also consistent with positron annihilation studies in PVAc³⁰ that propose an increase in total free-volume with increasing temperature above T_g , which involves growth of the hole sizes and primarily an increase in the number of holes, upon increasing temperature below T_g .

From these results we can consider that amorphous polymer matrices contain a distribution of sites with different free-volumes where AN molecules may be localized

and have different rates of non-radiative deactivation processes.

Energy transport of AN in polymer matrices

Following schemes proposed by Birks¹⁵ under steady-state conditions and where intersystem crossing terms are negligible, the fluorescence quantum efficiency is described by:

$$q_{FM} = k_{FM} / \{k_{FM} + k_{IM} + k_{QM} [Q] + k_{YM} [Y] + k_{DM} [M]\} \quad (2)$$

where the rate constants are: k_{FM} for fluorescence emission of the isolated molecule; k_{IM} for radiationless internal conversion; k_{QM} for collisional impurity quenching; k_{YM} for energy transfer quenching between two different molecules, a non-collisional radiationless energy transfer; k_{DM} for concentration quenching, a self quenching process of the $^1M^*$ fluorescence, which may result either in excimer or in dimer formation. The rate constants for the radiationless internal conversion processes k_{IM} are always composed of two terms: one temperature-dependent, k_{IM}^T and one temperature-independent, k_{IM}^0 .

Considering that at low temperatures there is no collisional impurity quenching in the polymer network, no energy transfer quenching (due to the absence of impurities whose absorption spectra overlap the fluorescence of M), and no concentration quenching in very dilute systems, Eq. 2 may be reduced to:

$$q_{FM} = k_{FM} / \{k_{FM} + k_{IM}^0 + k_{IM}^T\} \quad (3)$$

and is related to the fluorescence intensity I_F . These assumptions are realistic for the systems studied in this work at low temperatures since absorption by the homopolymers (in the ultraviolet region) is localized far from the emission of AN. In addition, if the intensity of the vibronic band of the AN molecules centered at ~380 nm is higher than that centered at ~402 nm, the self-quenching process is also negligible.

In the case of molecules dissolved in a rigid polymer at low temperatures, there is a probability of radiationless energy migration between two neighbouring molecules of the same species whose efficiency is controlled by the rate constant k_{MM} . In this case, two mechanisms for the quenching processes have been proposed: a) a dynamic collisional quenching process; and b) static quenching by a Foerster mechanism. In rigid media and in the absence of diffusion, static quenching has a higher probability than collisional quenching, and the efficiency of the static quenching process may be described by:

$$\epsilon_{ef} = R^6_0 / (R^6_0 + r^6) \quad (4)$$

All the terms of this equation have been described earlier^{7-13,15} and the relevant aspect for this work is that the

efficiency of energy migration is dependent on the distance r between the AN donor and acceptor molecules.

Another important process that changes the fluorescence quantum yield and consequently the intensity of the emission is the radiative transfer of the excitation (named a trivial process) of the $^1M^*$ species, a molecule in the electronically excited singlet state. This process is common if there is an overlap between the 0-0 band of fluorescence and absorption spectra. This overlap is significant for AN, as shown in Fig. 1, and the radiative transfer produces a self-absorption and re-emission of part of the fluorescence, except in very dilute solutions or very thin films. It competes with the escape of the fluorescence from the species in the film and changes the observed fluorescence lifetime and quantum yield (Φ_{FM}) from their true values (q_{FM})¹⁵:

$$(\Phi_{FM}) = [q_{FM}(1 - a)] / (1 - a q_{FM}) \quad (5)$$

The parameter a is named the self-absorption parameter and depends on the overlap between the absorption spectrum $E(\nu)$ and the fluorescence spectrum $F(\nu)$; the molar concentration $[M]$ of the molecule in the electronic ground state; and the specimen thickness d . The parameter a is a measure of the radiative transfer probability given, approximately by:

$$a = (2.303 [M] d / q_{FM}) \int_0^{\infty} F(\nu)E(\nu)d(\nu) \quad (6)$$

Therefore, the relative intensities of the vibronic bands of AN centered at 380 nm and 402 nm are strongly dependent on both the radiative transfer energy (trivial process) and the radiationless energy migration. The first process depends on the specimen thickness and the light scattering inside the material, while the latter one depends on the distance between two AN neighbouring molecules. If these energy transfer processes are important, the relative intensity I_{380} / I_{402} should be low. From the spectra shown in Fig. 1, the self-absorption parameter is reduced and, as a result the quantum yield should be approximately the real one at a certain temperature. We have demonstrated that the magnitude of these effects may be modified during the relaxation processes of polymers and polymer blends and the modification is dependent on the dimension of the macromolecular segments involved in the relaxation processes. These cooperative polymer-probe effects were used to determine relaxation temperatures of polymers as well as to establish the dimensions of the macromolecular segments participating in the relaxation⁷⁻¹¹.

In order to explain these effects, we have to consider the following possibilities:

1. During the relaxation process, there is a fluctuation of the thermal expansion coefficients that induces a fluctuation of the density, which modifies the probability of the light scattering inside the material³¹. If the relaxation proc-

ess reduces the light scattering probability, the pathway that the fluorescence photon must travel inside the material is shorter because one reduces the probability of multiple reflections and, as a consequence, the distance d . In this case the self-absorption parameter is reduced and as a result, the quantum yield is similar to the real one at a specific temperature. The magnitude of this effect also depends on the size of the macromolecular segments involved with the relaxation process of the polymer. Therefore, the modification of the light scattering probability inside the material changes its refractive index and consequently changes the probability of the energy migration by trivial radiative process.

2. As pointed out by Kauzmann³², while the volume $[V = (\partial G / \partial P)_T]$ is unchanged at the temperature of the relaxation process, the coefficient of thermal expansion $\alpha_V = (1/V) (\partial^2 G / \partial P \partial T)$ does undergo a rather sudden change. The magnitude of this bulk expansion is dependent on the size of the macromolecular segment involved in the polymer relaxation, producing an expansion of the material, and consequently the distance between two molecules dissolved in the medium increases. If there is a significant expansion of the material, the increase of the distance between two molecules will increase reducing the probability of the radiationless energy migration and the intensity of the fluorescence emission increases.

3. However, if there is an increase in the available free-volume or a production of new holes, the probability of the deactivation process by internal conversion mechanisms is higher and the intensity of fluorescence should be reduced.

Therefore, the final fluorescence intensity is a result of these three effects:

- i) trivial energy transfer;
- ii) radiationless energy migration;
- iii) internal conversion mechanism.

Typical curves for fluorescence intensity of AN dissolved in LDPE and PVAc as a function of temperature are shown in Fig. 3. The changes of their slopes correspond to a relaxation of the polymer chains and may be interpreted by changes of the photophysical deactivation mechanisms of the molecular probes.

As shown earlier, AN molecules dissolved in both polymers were present in isolated form, as shown by the fluorescence spectra (Figs. 1 and 2). Therefore, any consideration about the deactivation processes of this molecule dissolved in polymer matrices may be done using Eq. 3, for the true value of the quantum yield, while for microheterogeneous material, for which light scattering is always present, Eqs. 5 and 6 are also important.

The curve for the integrated intensity vs. temperature for fluorescence of AN dissolved in PVAc (Fig. 3□) exhibits two inflections at ~ 180 -200 K and ~ 304 K. The lower temperature is attributed to the β relaxation process of

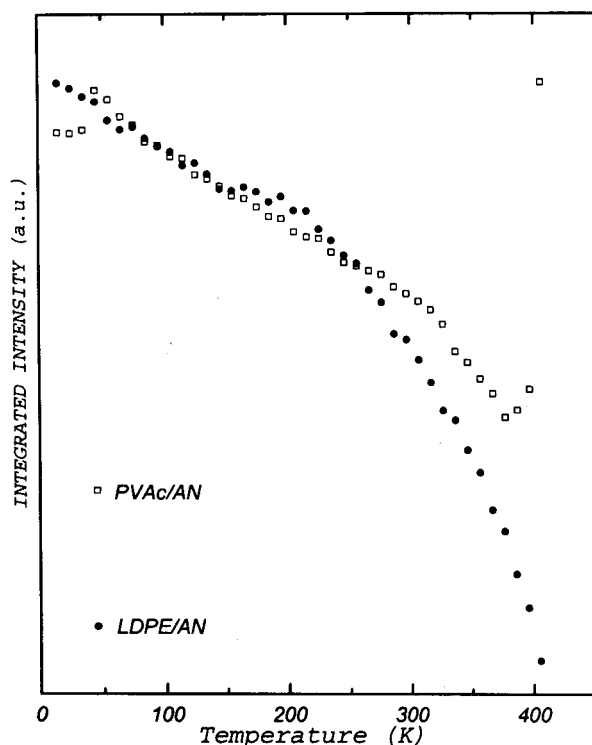


Figure 3. Normalized integrated intensity of the fluorescence band vs. temperature of AN dissolved in LDPE (●) and in PVAc (□).

PVAc and was also observed by photoluminescence using a phosphorescent molecular probe³³ and by dynamic mechanical spectroscopy³⁴. This process is believed to be characteristic of amorphous packings and may involve small amplitude rotational motions of one or two monomeric units, with an apparent activation energy around 20 kcal/mol. The small change of the slope of the fluorescence intensity curve in this temperature range is consistent with this model, since it is expected that motions of small segments of the polymer chains do not change appreciably non-radiative photophysical processes of the molecular probes (like internal conversion mechanisms, extrinsic energy migration, or even trivial energy transfer processes). The other inflection of the curve is much more pronounced and may be associated with the PVAc glass transition, which has also been observed using different techniques, such as dielectric relaxation, thermal stimulated current depolarization^{35,36}, differential scanning calorimetry, and photochemical reactions²⁹. This relaxation process involves an apparent activation energy of 138 kcal/mol, and is composed of two barriers: one for frictional resistance to the macromolecular motions and the other for conformational changes of the macromolecules. Polymer relaxation processes involving long segments of macromolecular chains induce diffusion of molecular probes (and consequently change the probability of the radiationless energy migration), produce significant in-

crease of the size and distribution of free-volumes (and consequently increase the efficiency of internal conversion processes), and reduce the light scattering by the material (which increases the efficiency of the excitation processes, reduces the magnitude of the self-absorption parameter, and results in the apparent quantum yield being closer to the real one). This last process may explain the increase of the fluorescence intensity for $T > 370$ K.

In the case of AN dissolved in LDPE, the curve for integrated fluorescence intensity vs. temperature (Fig. 3●) shows three segments with different slopes: a) from 15 - 150 K, we are observing a continuous decrease of the fluorescence intensity as the temperature increases. Diffusion of AN molecules in this temperature range is not expected and, consequently, radiationless energy migration processes should be constant. Therefore, the two most important deactivation processes should be internal conversion and trivial energy transfer. At ~ 150 K, there is a set of relaxation processes of polyethylene, named relaxations, which involve motions of small segments of the polymer chains and which are associated to different domains of the matrix, such as amorphous interlamellar regions, lamellae surfaces and interface amorphous-crystalline regions⁸. b) The segment of the curve from 150 K to 230 K presents a lower slope than the lower temperature range. There are motions of small segments of LDPE chains at $T > 150$ K which produce different types of photophysical effects for the deactivation of AN, such as: an increase of the efficiency of internal conversion processes, that reduce the fluorescence intensity; a reduction of the efficiency of radiationless energy migration, due to the expansion of the free-volume of the system; and a decrease of the yield of trivial migration process by the density fluctuation during the relaxation processes. All of these effects, with opposite tendencies, reduce the slope of the curve from $150 \leq T \leq 230$ K. This last temperature, attributed to the polyethylene β relaxation process, was determined by several methods. It involves long segments of polymer chains and, consequently, produces a significant increase of non-radiative deactivation processes of AN in the electronically excited singlet state. c) The last change of slope is observed at $T \sim 330$ K and this temperature may be attributed to the α relaxation process of polyethylene^{37,38}. Following the mechanisms proposed by Boyd³⁸, this relaxation is produced by the diffusion of defects through the polymer chains of both crystalline and amorphous phases. As shown earlier, AN molecules should be localized either in the totally amorphous phase or on the surface of the crystallites. Relaxation processes in this last case would produce significant changes in the photophysical properties of AN molecules, as actually observed in Fig. 3.

From all of these results we can conclude that AN probe molecules dissolved in amorphous or semi-crystalline polymers present a set of different photophysical properties

which are useful to map different types of polymer domains, as well as to follow their relaxation processes in the solid state.

Conclusions

It has been reported in this work that AN molecules dissolved in polymers present fluorescence spectra whose vibronic resolution is dependent on the dimensions and rigidity of the matrix free volumes, as in the case of crystalline or glassy solvents. Moreover, this molecule exhibits some types of energy transfer processes which change both the fluorescence intensity and the relative intensity of the fluorescence vibronic bands. These spectral characteristics are dependent on the concentration, temperature and interactions between host and guest species and these properties may be used to follow polymer relaxation processes.

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